Characterisation of weathering properties of "new generation" low sulphur fuel oils

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Introduction

In 2015, stricter IMO regulations regarding content of sulphur in marine fuel oils used within the "Sulphur Emission Control Areas" (SECA-zones) were implemented, and further changes have been scheduled globally for 2020 (MARPOL Annex VI). These changes in regulations have resulted in an increased production of a "new generation" of low sulphur fuel oils with properties that make them suitable for use in existing heavy fuel engine vessels. These oil types show properties form both light distillate fuels and heavier fuel qualities, and may be difficult to classify within existing ISO-standards. In addition, the weathering properties of these fuel oil types have not previously been tested with respect to consequences for oil spill operations.

SINTEF and the Norwegian Coastal Administration (NCA) have cooperated on a study of three "new generation" low sulphur fuel oils, Shell's Ultra Low Sulphur Fuel Oil (here called ULSFO), ExxonMobil's Heavy Distillate Marine ECA 50 (HDME 50), and Mongstad's Wide Range Gas oil (WRG), as well as three DMA-quality diesel fuel oils (here called MGO, GO and Rotterdam diesel). These products have been tested with respect to weathering behaviour and properties relevant for potential response operation in Nordic and Arctic temperatures (sea temperatures of 2-13 °C). Properties related to mechanical recovery have been tested in the oil spill test basin at NCA's National Centre for Testing of oil, using different response equipment, e.g. various skimmer types. SINTEF has investigated the weathering properties, including studies of the oil's physical and chemical properties, their emulsifying properties, dispersibility, ignitability, and the chemical composition of water accommodated fraction (WAF) and its toxicity on two marine species. In addition, testing in the SINTEF meso-scale flume has been performed for WRG, MGO, HDME 50 and ULSFO. This paper summarised the main results from the tests performed by SINTEF (Hellstrøm and Daling, 2017; Hellstrøm *et al.*, 2017).

Main Results

Bench-scale studies of the chemical composition, physical properties and emulsifying properties were performed for above mentioned six marine fuel oils. Of the three "new generation" fuel oils, ULSFO is a residual fuel oil with a broad spectre of both lighter and heavier components (C_9-C_{40}), while HDME 50 is a heavy distillate cut (C_{15}-C_{55}) (see Figure 1). The WRG is also a heavy distillate cut (C_{12}-C_{35}), while the tested DMA-qualities consisted of lighter components in the C_9-C_{25} range.

For each of the six fuel oils, the chemical composition of the water-soluble fraction (WSF or WAF – water accommodated fraction) was investigated, and the toxicity of the respective WAFs was tested using two marine organisms, the algae *Skeletonema sp*. and the copepod *Calanus finmarchicus*, which represent two different trophic levels in the marine ecosystems. Of the tested oils, the WAF from Rotterdam diesel caused the highest toxic effect, likely caused by a high content of light polycyclic aromatic (and toxic) hydrocarbons (PAHs) (see Figure 2). The other two DMA-qualities, GO and MGO, had more similar chemical compositions, and was not found to cause the same degree of toxic effects. ULSFO, HDME 50 and WRG had low content of water soluble components and caused little toxic effect (Figure 2).

Using rotating cylinders, WRG, HDME 50 and ULSFO were found to express different degrees of emulsifying properties, with varying emulsion viscosity and stability, while the DMA-qualities did not show emulsifying properties due to lack of heavier asphaltenic and waxy components. ULSFO and HDME 50 had high wax content and presence of asphaltenes and formed stable emulsions at all test temperatures, but varying water content and temperature dependent emulsion viscosities. WRG formed unstable emulsions due to lack of asphaltenes and presence of wax, and in general low emulsion viscosities. Due to their high wax content, ULSFO and WRG had high pour points.

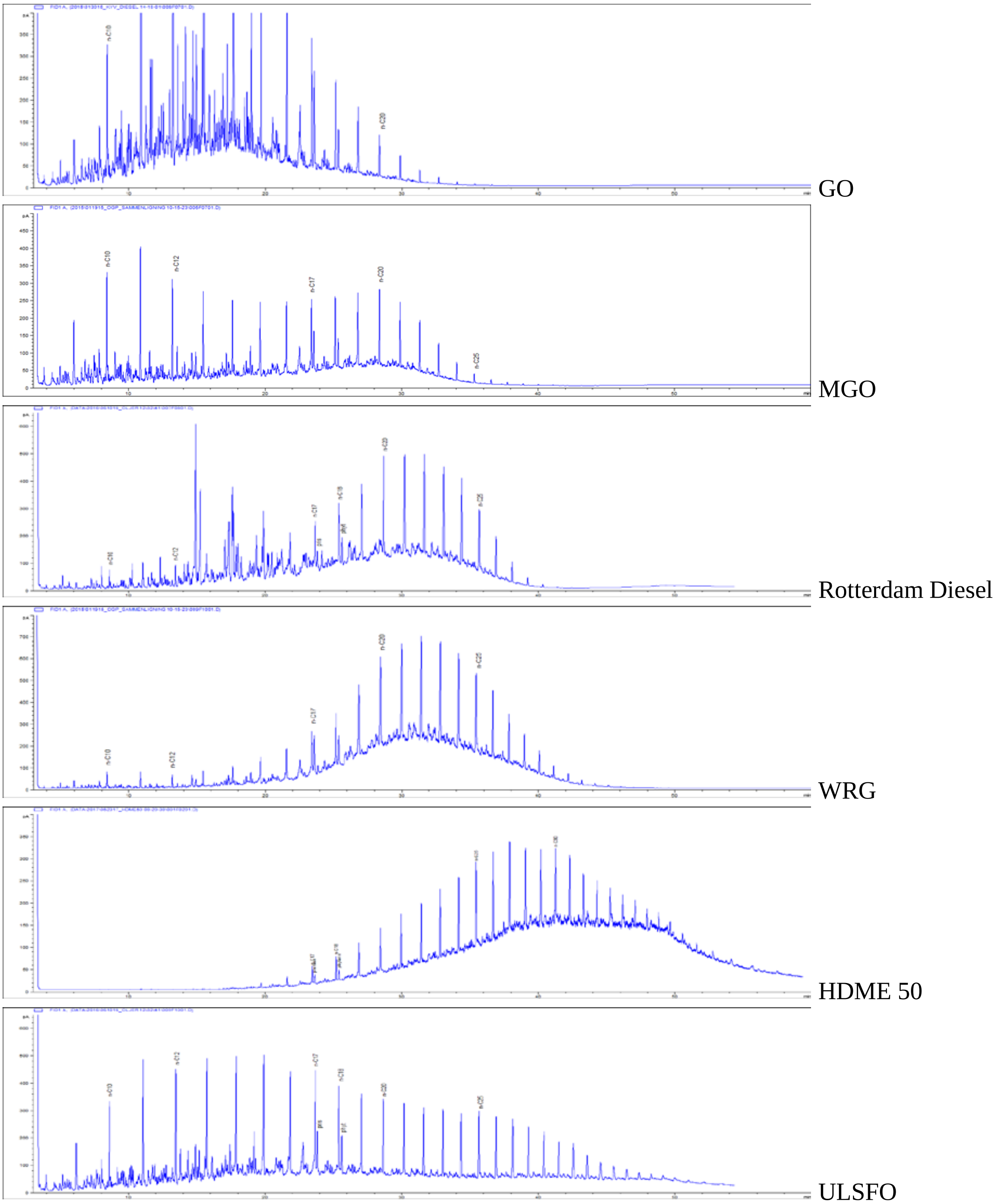

Figure 1: GC-FID chromatograms of the six tested fuel oils

A screening of six different oil spill dispersants (Dasic Slickgone NS, Corexit 9500, Finasol OSR-52, Superdispersant, Gamlen OD 4000 and Radiagreen) were performed for all the fuel oils, using the Institute Francais du Petrole (IFP) dispersant methodology. ULSFO, HDME 50 and WRG were subjected to further systematic dispersibility testing using Dasic NS and both the IFP- and MNS-methodologies (representing calm and breaking wave conditions, respectively) at two test temperatures (2 and 13 °C). The results showed temperature dependent dispersibility for these oils, with poor dispersibility at lower temperatures. The high pour points of ULSFO and HDME 50 contributed largely to this behaviour. In a response operation, chemical dispersants should be applied as soon as possible while emulsion viscosities are at their lowest. The test results also showed that repeated application of dispersant was more effective on these fuel oils compared to application of a single high dose. In general, application of additional energy (e.g. use of high capacity water flushing) in calm sea conditions will likely enhance the dispersion of the treated oil/emulsion.

Due to their high pour points, HDME 50 and ULSFO may solidify on the sea surface, and form solid lumps. In the meso-scale testing the emulsion viscosities were measured up to 50 000 mPa·s at 2 °C, indicating that high viscosity skimmers may be required for effective recovery of the oil/emulsion.

For testing the potential for use of *in*-situ burning, the ignitability of the six fuel oils were investigated using SINTEF's Burning Cell, a bench-scale test, and upscaled testing outdoors, using up to 5 L of oil in a water-filled metal tray. Of the oils, ULSFO and MGO ignited most easily, followed by GO and Rotterdam diesel. As previously mentioned, WRG and HDME 50 were heavy distillate cuts, and these oils did not ignite in the bench-scale testing. However, in the up-scaled outdoor tray testing these oils ignited after prolonged ignition time.

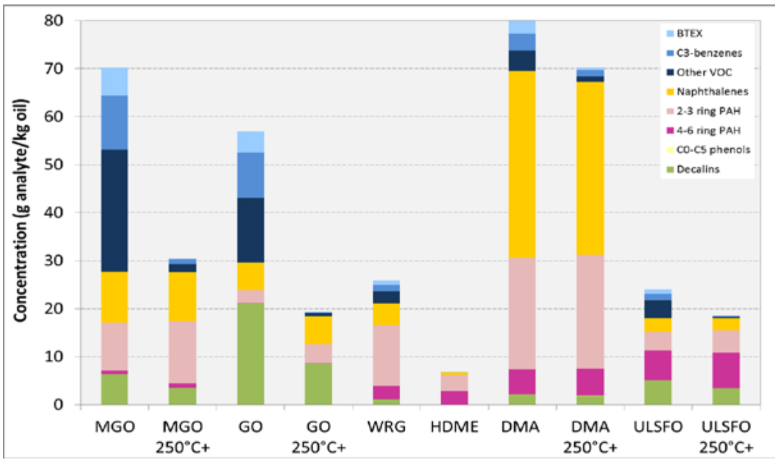

Figure 2: Chemical composition of selected component groups (aromatics) in the six fuel oils and their artificially weathered fractions

Conclusion

The tested DMA-qualities exhibited similar physical properties and weathering behaviour, but significantly different chemical compositions of oil and WAF, and different toxicity.
The three "new generation" low sulphur fuel oils ULSFO, HDME 50 and WRG, have distinctly different weathering behaviour and weathering properties. However, for all three oils, sea temperature highly affected these properties.
Chemical dispersion of the "new generation" fuel oils may have limited effect due to high pour point values, particularly in colder temperatures.
In-situ burning may have potential under special circumstances where spreading and emulsification is prevented, though long ignition time is expected for WRG and HDME 50

It is important to continue the testing of "New generation" fuel oils to gain better understanding of their fate and behaviour in a release situation. This knowledge is vital to make the best choices for response operations, particularly for Northern regions, considering the observed temperature dependent behaviours.

References

Hellstrøm, K. C., Daling, P. S., Brönner, U., Sørheim, K. S., Johnsen, M., Leirvik, F. and Altin, D., 2017. Memo report: Collection of project memos. SINTEF report no.: OC2017-A123. ISBN: 9788271742980
Hellstrøm, K. C. and Daling, P. S., 2017. Weathering properties and toxicity of marine fuel oils. SINTEF report no.: OC2017-A124. ISBN: 9788271742997